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## MANUFACTURE OF AROMATIC CARBONIC ESTERS

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Abstract

## Objective

To offer a method for manufacturing aromatic carbonic esters.

## Means

An aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide in the presence of catalyst to manufacture an aromatic carbonic ester, where the reaction is carried out in the presence of (A) palladium or a palladium compound, (B) copper compound or lanthanide compound, (C) 2-hydroxypyridines and (D) aprotic polar solvent.

## Claims

1. A method for manufacturing aromatic carbonic esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide in the presence of a catalyst; said method for manufacturing aromatic carbonic esters being characterized in that said reaction is allowed to occur in the presence of (A) one or more types of substance selected from palladium and palladium compounds; (B) one or more types of substance selected from copper compounds and lanthanoid compounds; (C) one or more types of substance selected from among 2-hydroxypyridines and (D) an aprotic polar solvent.
2. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein said aprotic polar solvent is at least one substance selected from an amide, ether or sulfoxides.
3. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the aprotic polar solvent is used in the range of 0.1-100 mol per mole of the aromatic hydroxy compound.

4. The method for manufacturing aromatic carbonic esters according to Claim 1, where the reaction is carried out in the co-presence of organic acid.

5. The method for manufacturing aromatic carbonic esters according to Claim 4, wherein the organic acid is acetic acid.

6. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the 2-hydroxypyridine substance is 2-hydroxypyridine.

7. The method for manufacturing aromatic carbonic esters according to Claim 1, wherein the aromatic hydroxy compound is phenol.

#### Detailed description of the invention

[0001]

#### Technological field of the invention

The present invention concerns a method for manufacturing aromatic carbonic esters using a special catalyst. Aromatic carbonate esters, particularly diphenyl carbonate, is useful as a raw material for producing polycarbonate.

[0002]

#### Prior art

Known methods for the manufacture of aromatic carbonic esters that have been used in the past include methods wherein an aromatic hydroxyl compound and phosgene are allowed to react, and

a method wherein an aliphatic carbonic ester and aromatic hydroxyl compound are allowed to undergo transesterification. The former method is undesirable because phosgene is a toxic substance, and a large amount of alkali is required in order to neutralize the hydrogen chloride that is a by-product. The latter reaction is essentially a two-stage reaction comprising the manufacture of aliphatic carbonic ester as well as the manufacture of aromatic carbonic ester, and thus is undesirable from an industrial standpoint. Moreover, the equilibrium of the reaction tends towards the side of the raw materials, and thus adequate yields and reaction rates are not obtained. Consequently, a method for the direct manufacture of aromatic carbonic esters from an aromatic hydroxyl compound, carbon monoxide and oxygen have been offered.

[0003]

A method is disclosed in Japanese Kokoku Patent No. Sho 56[1981]-38143 and Japanese Kokai Patent Application No. Sho 53[1978]-68747, wherein palladium complex is allowed to react with phenol and carbon monoxide in the presence of base. However, this reaction is not a catalytic reaction, and requires stoichiometric quantities of palladium, which is a disadvantage from the standpoint of industrial utilization.

[0004]

A method that employs palladium at below stoichiometric amounts is described in Japanese Kokoku Patent No. Sho 56[1981]-38144, but this method does not produce sufficient

reactivity for industrial use. In addition, there are problems with the selectivity of the reaction that produces the carbonate. A revised method wherein a desiccant is added is described in Japanese Kokoku Patent No. Sho 56[1981]-38145, and although the reactivity was increased, the method is not amenable to industrial utilization due to the increase in complexity resulting from carrying out the reaction in the presence of a large quantity of desiccant. In addition, regenerating the desiccant is costly, which is a disadvantage from an industrial standpoint.

[0005]

In order to improve reactivity, methods are described in Japanese Kokai Patent Application No. Sho 54[1979]-135743, Japanese Kokai Patent Application No. Sho 54[1979]-135744, Japanese Kokai Patent Application No. Hei 2[1990]-104564, Japanese Kokai Patent Application No. Hei 2[1990]-142754, Japanese Kokai Patent Application No. Hei 6[1994]-9505, Japanese Kokai Patent Application No. Hei 6[1994]-211750, Japanese Kokoku Patent No. Hei 6[1994]-57678, Japanese Kokai Patent Application No. Hei 6[1994]-172268, Japanese Kokai Patent Application No. Hei 6[1994]-172269, Japanese Kokai Patent Application No. Hei 6[1994]-271506 and Japanese Kokai Patent Application No. Hei 6[1994]-271509, wherein, in addition to catalyst and auxiliary catalyst, quinones and tetraalkylammonium halide or alkali metal or alkaline earth metal halides are added in large quantities. Not only is recovery of these compounds difficult, but the presence of high halogen concentrations (chlorine, bromine, iodine, fluorine) causes corrosion of the reaction equipment,

necessitating high-grade materials for the reaction equipment. Such methods are thus disadvantageous due to high costs from the standpoint of the entire process.

[0006]

Japanese Kokai Patent Application No. Hei 1[1989]-165551 discloses a more simple catalytic system wherein an auxiliary catalyst is not used. Even with this system, however, large amounts of iodine compound salt are used in addition to the primary group VIII of metal catalyst, which leads to problems similar to those described above resulting from the use of high halogen concentrations. The use of a compound that contains halide ions as an additive is a characteristic of each of these catalyst systems having comparatively high activities that have been used in these conventional methods for manufacturing aromatic carbonic esters by means of a reaction between oxygen and an aromatic hydroxy compound and carbon monoxide. On the other hand, a method that does not employ a halogen compound has been offered in Japanese Kokai Patent Application No. Hei 6[1994]-41020, where aromatic carbonic esters are manufactured using a nitrile solvent.

[0007]

Problems to be solved by the invention

However, although methods that do not employ halides have comparatively good initial reaction performance, it is necessary to recover and regenerate the catalyst components, which is

disadvantageous from an industrial standpoint. The objective of the present invention is to offer a method for manufacturing aromatic carbonic esters using a catalyst by allowing an aromatic hydroxy compound to react with carbon monoxide and oxygen to produce aromatic carbonate esters, where the reaction progresses at industrial-level reaction rates, without using quinones or halides.

[0008]

Means to solve the problem

The inventors of the present invention, as a result of painstaking investigations towards a solution to the problems described above, arrived at the present invention upon discovering that when a reaction is carried out in the presence of a conventional palladium catalyst, while using an aprotic polar solvent and 2-hydroxypyridines in an auxiliary catalyst system, the reaction progresses at industrial-level reaction rate without the generation of halide by-products, as has occurred in the past. Specifically, the present invention is a method for manufacturing aromatic carbonic esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide in the presence of catalyst, said method for manufacturing aromatic carbonic esters being characterized in that said reaction is allowed to occur in the presence of (A) one or more types of substance selected from palladium and palladium compounds, (B) one or more types of substances selected from copper compounds and lanthanoid compounds, (C) one or more types of substances selected from among 2-hydroxypyridines and (D) an



aprotic polar solvent. The method of the present invention is described in detail below.

[0009]

#### Embodiment of the invention

##### 1. Raw materials

###### (1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention can be any substance, provided that it is an aromatic mono- or polyhydroxy compound whose hydroxyl groups are bonded directly to an aromatic ring. Examples include phenol, cresol, xlenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol, methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, dibromophenol and other substituted phenols and isomers thereof; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol and other substituted naphthols and other related compounds; 2,2'-bis(4-hydroxyphenyl)propane and various other types of bisphenols; various types of biphenols, and other compounds. Phenol is particularly desirable among these substances.

[0010]

###### (2) Carbon monoxide

The carbon monoxide that is used in the present invention can be a gas that is produced by starting with high-purity substance and diluting it with another gas that does not have a

detrimental influence on the reaction, such as nitrogen, argon, carbon dioxide or hydrogen.

[0011]

### (3) Oxygen

The oxygen gas that is used in the present invention can be produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as air, nitrogen, argon, carbon dioxide or hydrogen.

[0012]

## 2. Catalyst

The catalyst that is used in the reaction comprises the three components (A)-(C) listed below.

### (A) Palladium or palladium compound

The palladium or palladium compound that is used in the present invention is palladium black, palladium carbon, palladium/alumina, palladium/silica or other carried palladium; palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salt; and palladium acetate, palladium oxalate or other organic palladium acid salt. In addition, substances that can also be used include palladium (II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on palladium, examples of which include  $\text{PdCl}_2(\text{PhCN})_2$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{CO})(\text{PPh}_3)_3$ ,  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$  and  $\text{Pd}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ , or mixtures of palladium and compounds

produced in the reaction system from these complexes. In addition, bis(2-hydroxypyridinate)palladium chloride produced using palladium chloride alkali metal salts (for example,  $\text{Na}_2\text{PdCl}_4$ ) and 2-hydroxypyridine can be prepared beforehand and used in the reaction. The palladium component that is used in the reaction is preferably used in the range of  $10^{-2}$  to  $10^{-5}$  mol per mole of aromatic hydroxy compound, with a range of  $10^{-3}$  to  $10^{-4}$  moles being preferred.

[0013]

(B) Auxiliary catalyst

The substance that is used as auxiliary catalyst in the present invention is one or more types of substance selected from among copper compounds and lanthanoid compounds, and if various metal ions are present, there are no particular restrictions on the type of counter-ions that are used. Examples of copper compounds include copper acetate, copper formate, copper benzoate, copper (I) chloride, copper (II) chloride, copper (I) bromide, copper (II) bromide, copper (I) iodide, copper (II) iodide, copper nitrate, copper hydroxide, and copper acetylacetonate. Examples of lanthanoid compounds include cerium acetate, cerium chloride, cerium bromide, lanthanum acetate and praseodymium acetate. The aforementioned copper compounds can be used individually, but it is preferable for two or more types of the former and latter substances to be used in conjunction. It is additionally desirable if copper acetate and cerium acetate are used simultaneously. The used amount of the aforementioned auxiliary catalyst is selected from ratios within a range of 0.5-1000 mol per mole of the aforementioned palladium component

(A), with 1-600 mol being preferred. If this ratio is less than 0.5x by mole, a smooth catalytic reaction will not be maintained, and the catalyst component will readily sediment, making it difficult to maintain high activity. If the ratio is 1000x by mole or greater, on the other hand, the production of undesirable by-products will be facilitated, and the use of such an amount is also undesirable from an economic standpoint.

[0014]

(C) 2-Hydroxypyridines

The 2-hydroxypyridines that are used in the present invention are 2-hydroxypyridine and related compounds that have substituents on a 2-hydroxypyridine backbone which do not interfere with the reaction, examples of which include compounds having alkyl groups, alkoxy groups, or a chlorine, bromine, fluorine or other halogen atom. Specific examples include 2-hydroxypyridine, 2-hydroxy-4-methylpyridine, 2-hydroxy-6-methylpyridine, 2-hydroxy-4-ethylpyridine, 2-hydroxy-4-methoxypyridine, 2-hydroxy-6-methoxypyridine, 4,6-dimethyl-2-hydroxypyridine, 2-hydroxy-4-chloropyridine and 2-hydroxy-6-chloropyridine. 2-hydroxypyridine and 2-hydroxy-6-methylpyridine and other 2-hydroxyalkylpyridines are preferably used. Moreover, the same is true of the alkali metal salts and other salts of these compounds. There are no particular restrictions on the amount of 2-hydroxypyridine that is used in the invention, but it is preferable to use an amount that is in the range of 0.1-100 mol per mole of palladium component (A), with a range of 1-10 mol being preferred. The aforementioned three components (A), (B) and (C) can be used after dissolving

them in solvent together with the hydroxy compound to produce a uniform solution, or one or all of the three components can be carried on a carrier such as activated carbon, silica or a polymer, and used as an immobilized catalyst.

[0015]

### 3. Solvent ((D) aprotic solvent)

The aprotic solvent that is used in the present invention is an oxygen-containing organic compound, sulfur-containing organic compound, nitrogen-containing organic compound or phosphorus-containing organic compound. Specific examples include nitrogen-containing compounds such as amides, for example, dimethylformamide, N-methylformamide and N-methyl-2-pyrrolidone, but examples are not limited to these. Examples of oxygen-containing compounds include ketones such as acetone and methyl ethyl ketone; esters such as ethyl acetate and methyl acetate; aldehydes such as acetaldehyde; ethers such as tetrahydrofuran and 1,4-dioxane; and lactones such as  $\gamma$ -butyrolactone and valerolactone, but examples are not restricted to these substances. Examples of phosphorus-containing compounds include hexamethylphosphoramide, hexamethylphosphoric triamide, triethylphosphite, tributylphosphine oxide, and triethylphosphine, but examples are not limited to these substances. Examples of sulfur-containing compounds include carbon disulfide, dimethylsulfoxide, sulfolane, tetramethylenesulfone, thiophene, dimethyl sulfide or mixtures thereof, but examples are not limited to these. It is preferable to use a nitrogen-containing organic compound in the present invention, with dimethylformamide being particularly desirable.

The used amount of the aforementioned solvent is not specifically restricted in terms of its ratio, and the ratio of the solvent can be freely determined. However, a range of 0.1-100 mol per mole of phenol is generally used, with about 1-10 mol being preferred.

[0016]

In order for the reaction to progress with good efficiency, it is desirable to carry out the reaction in combination with any acid, particularly an organic acid. Examples of acids include carboxylic acids, sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, trienesulfonic acid, trifluoroacetate and heteropolyacids. Specific examples of carboxylic acids include acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, pivalic acid, monochloroacetic acid and other aliphatic carboxylic acids, and benzoic acid and other aromatic carboxylic acids. Acetic acid is particularly desirable. The amount of acid used depends on the type of acid, but ordinarily, 1-1000 mol per mole of the palladium component (A) is used, with a range of 10-100 mol being particularly desirable.

[0017]

#### 4. Reaction conditions

There are no particular restrictions on the reaction temperature, which is ordinarily 50-200°C, with 80-140°C being preferred. If the reaction temperature is less than 50°C, then a sufficient reaction rate will not be obtained. If the reaction temperature is greater than 200°C, on the other hand,

side-reactions will readily occur. The reaction pressure can be selected appropriately from within a range of ambient pressure to 100 atm based on economic considerations. The oxygen partial pressure is preferably 0.5-5 atm, with a range of 1-2 atm being additionally desirable. The carbon monoxide partial pressure is preferably 10-70 atm, with a range of 20-50 atm being additionally desirable. The format of the reaction may be a batch format, semi-batch format or continuous format.

[0018]

#### Application examples

The method of the present invention is described in detail below by providing application examples, but the present invention is not restricted to these application examples.

[0019]

#### Application Example 1

5.0 g (53.1 mmol) of phenol, 4.4 mg (0.012 mmol) bis(2-hydroxypyridine)palladium chloride, 18 mg (0.1 mmol) of copper (II) acetate, 34 mg (0.1 mol) of cerium (III) acetate monohydrate, 0.064 mL (1 mmol) of acetic acid, 24 mg (0.25 mmol) of 2-hydroxypyridine and 5 mL of dimethylformamide were introduced into an autoclave with an inner volume of 70 mL, and after replacing the interior of the system with carbon monoxide, the system was pressurized at room temperature with 40 kg/cm<sup>2</sup> carbon monoxide, and 60 kg/cm<sup>2</sup> of oxygen gas diluted with

nitrogen gas (3.7 vol% oxygen). A reaction was allowed to occur for 0.5 h at 120°C while stirring with a magnetic stirrer, and the contents were then analyzed by gas chromatography. The results indicated a diphenyl carbonate yield of 4.7 % (1.24 mmol). The turnover number of the reaction (referred to below as "TON") was 103 mol/mol-Pd.

[0020]

#### Application Examples 2-7

A reaction was carried out by the same method as in Application Example 1, with the exception that the 5 mL of dimethylformamide was changed to dimethylacetamide, diethylacetamide, dimethylsulfoxide, N-methyl-2-pyrrolidone, sulfolane,  $\gamma$ -butyrolactone, tetrahydrofuran and 1,4-dioxane and 1,1,3,3-tetramethylurea. The results are collated in Table I.

[0021]

#### Comparative Example 1

A reaction was carried out by the same method as in Application Example 1, with the exception that the dimethylformamide was changed to phenol. The results are shown in Table I.



[0022]

Comparative Example 2

A reaction was carried out by the same method as in Application Example 1, with the exception that the dimethylformamide was changed to cyclohexane. The results are shown in Table I. As shown in Table I, the reaction did not progress catalytically in the absence of solvent or in non-polar solvent.

[0023]

Application Example 9

A reaction was carried out by the same method as in Application Example 1, with the exception that the carbon monoxide partial pressure was changed to 20 kg/cm<sup>2</sup> and the pressure of nitrogen-diluted oxygen gas (3.7 vol% oxygen) was changed to 80 kg/cm<sup>2</sup>. The diphenyl carbonate yield was 5.6% (1.5 mmol) in this reaction, with a TON of 126 mol/mol-Pd.

[0024]

Application Example 10

A reaction was carried out in the same manner as in Application Example 9, with the exception that 2.7 mg

(0.012 mmol) of palladium acetate was used. The diphenyl carbonate yield of this reaction was 2.6% (0.68 mmol), with a TON of 57 mol/mol-Pd.

[0025]

#### Application Example 11

A reaction was carried out in the same manner as in Application Example 9, with the exception that 3.2 mg (0.012 mmol) of palladium bromide was used instead of the bis(2-hydroxypyridine)palladium chloride complex. The diphenyl carbonate yield of the reaction was 5.2% (1.37 mmol) with a TON of 114 mol/mol-Pd.

[0026]

#### Application Example 12

A reaction was carried out in the same manner as in Application Example 9, with the exception that 26 mg of 5% palladium-carbon catalyst (manufactured by NE-kemukyatto [transliteration]) that had been washed with water and vacuum-dried was used. The results indicated that diphenyl carbonate was obtained at a yield of 1.8% (0.49 mmol), with a TON of 41 mol/mol-Pd.

Comparative Example 3

A reaction was carried out by the same method as in Application Example 1, with the exception that 2.1 mg (0.012 mmol) of palladium chloride was used instead of bis(2-hydroxypyridine)palladium chloride complex, and 2-hydroxypyridine was not added. The results indicated that diphenyl carbonate was obtained at a yield of 1.2% (0.31 mmol), with a TON of 26 mol/mol-Pd.

[0028]

Application Example 13

A reaction was carried out by the same method as in Application Example 1, with the exception that acetic acid was not added. The results indicated that diphenyl carbonate was obtained at a yield of 1.4% (0.36 mmol), with a TON of 30 mol/mol-Pd.

[0029]

Table I

//insert table I//

Key: 1	Number
2	Solvent (5 mL)
3	Product DPC <sup>*1</sup> (mmol)
4	DPC yield TON <sup>*2</sup> (%)
5	Comparative Example 1
6	Application Example 1
7	Phenol
8	Dimethylformamide
9	Dimethylacetamide
10	N-methyl-2-pyrrolidone
11	1,1,3,3-Tetramethylurea
12	Sulfolane
13	Dimethylsulfoxide
14	Tetrahydrofuran
15	Cyclohexane
16	<sup>*1</sup> Diphenyl carbonate

17    \*<sup>2</sup> Turnover number

[0030]

Effect of the invention

By means of the present invention, aromatic carbonic ester can be obtained at a high rate of reaction without using quinones, quaternary ammonium halides or alkali metal or alkaline earth metal halides.

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